

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 870 625 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

14.10.1998 Bulletin 1998/42

(51) Int Cl.⁶: **B41M 5/30**

(21) Application number: **98301953.0**

(22) Date of filing: **24.03.1998**

(84) Designated Contracting States:

**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **10.04.1997 US 835701**

(71) Applicant: **APPLETON PAPERS INC.
Appleton Wisconsin 54912 (US)**

(72) Inventors:

- **Cove, Michael Gerald
Neenah, Wisconsin 54956 (US)**
- **Schulz, Mary Ellen
Greenville, Wisconsin 54942 (US)**

(74) Representative: **Norris, Richard John
Intellectual Property Department,
Arjo Wiggins Appleton plc,
Butler's Court,
Wattleton Road
Beaconsfield, Buckinghamshire HP9 1RT (GB)**

(54) Thermally-responsive record material

(57) Thermally responsive record material comprises a support having provided thereon in substantially contiguous relationship in one or more layers an electron donating dye precursor, an acidic developer material, a sensitizer, and a binder therefor. The sensitizer comprises at least two components, the first component comprising 2,2-bis(4-hydroxyphenyl)-4-methylpentane and the second component comprising a mixture of

dimethyl terephthalate and 1,2-diphenoxyethane. The first component is preferably in a weight ratio of from 1:2 to 2:1, more preferably 1:1, relative to the second component. The second component comprises from 50 to 70% dimethyl terephthalate. The sensitizer is prepared by admixing the first component and the second component and grinding the sensitizer to a particle size of less than 1 micron.

Best Available Copy

EP 0 870 625 A1

Description

This invention relates to thermally-responsive record material, particularly in the form of sheets coated with color-forming systems comprising chromogenic material (electron-donating dye precursors) and acidic color developer material. This invention particularly concerns a thermally-responsive record material capable of forming a non-reversible image resistant to fade or erasure due to contact with oils, solvents or exposure to elevated temperature, and/or having improved image density retention.

Thermally-responsive record material systems are well known in the art and are described in many patents, for example, U.S. Pat. Nos. 3,539,375; 3,674,535; 3,746,675; 4,151,748; 4,181,771; 4,246,318; and 4,470,057. In such systems, basic chromogenic material and acidic color developer material are contained in a coating on a substrate which, when heated to a suitable temperature, melts or softens to permit said materials to react, thereby producing a colored mark.

Thermally-responsive record materials have characteristic thermal responses, desirably producing a colored image of sufficient intensity upon selective thermal exposure.

Thermally-responsive record materials in certain environments and applications have the undesirable tendency upon forming an image to not retain that image in its original integrity over time when the thermally-responsive record material is handled or exposed to common liquids or oils or plasticizers such as found in skin oil, plastic food wrap, cooking oil and solvents such as common carbonless paper solvents. Resistance to fade or more intense imaging is desirable.

The ability of a thermally-responsive record material to resist image fading or erasure upon contact with common oils, solvents or plasticizers or to have improved image density and/or faster imaging would be an advance in the art and of commercial significance. It is an object of the present invention to provide a thermally-responsive record material which is improved in one or more of these respects and which comprises a support member bearing a thermally-sensitive color forming composition comprising chromogenic material and acidic developer material in substantially contiguous relationship, whereby the melting or sublimation of either material produces a change in color by reaction between the two, a suitable binder therefor also being present.

According to a first aspect of the present invention, there is provided a thermally responsive record material comprising a support having provided thereon in substantially contiguous relationship in one or more layers an electron donating dye precursor, an acidic developer material, a sensitizer, and a binder therefor, characterized in that the sensitizer comprises at least two components, the first component comprising 2,2-bis(4-hydroxyphenyl)-4-methylpentane (AP5) and the second component comprising a mixture of dimethyl terephthalate (DMT) and 1,2-diphenoxyethane (DPE), said second component comprising from 50 to 70% dimethyl terephthalate by weight, and in that the sensitizer is prepared by admixing the first component and the second component and grinding the sensitizer to a particle size of less than 1 micron.

In a second aspect, the present invention provides a process for forming an improved sensitizer for thermally responsive record material comprising admixing a first component and a second component, the first component comprising 2,2-bis(4-hydroxyphenyl)-4-methylpentane and the second component comprising a mixture of dimethyl terephthalate and 1,2-diphenoxyethane, said second component comprising from 50 to 70% dimethyl terephthalate by weight, grinding the admixture to a particle size of less than 1 micron, and forming an aqueous slurry of the admixture.

The first sensitizer component is preferably in a range of weight ratios from 1:2 to 2:1, more preferably 1:1, relative to the second component.

By grinding the sensitizer components together in the above-described weight ranges, a surprising improvement in image intensity and/or thermal response was detected. This improvement was not detectable when the components were ground separately or mixed in weight ranges outside the above-described weight ranges.

The record material according to the invention has a non-reversible image in that it is substantially non-reversible under the action of heat. The coating of the record material of the invention is basically a dewatered solid at ambient temperature.

The color-forming system of the record material of this invention includes chromogenic material (electron-donating dye precursor) in its substantially colorless or light-colored state and acidic developer material. The color-forming system relies upon melting, softening, or subliming one or more of the components to achieve reactive, color-producing contact with the chromogen.

The record material includes a substrate or support material which is generally in sheet form. For purposes of this invention, sheets can be referred to as support members and are understood to also mean webs, ribbons, tapes, belts, films, cards and the like. Sheets denote articles having two large surface dimensions and a comparatively small thickness dimension. The substrate or support material can be opaque, transparent or translucent and could, itself, be colored or not. The material can be fibrous including, for example, paper and filamentous synthetic materials. It can be a film including, for example, cellophane and synthetic polymeric sheets cast, extruded, or otherwise formed. The invention resides in the color-forming composition coated on the substrate. The kind or type of substrate material is

not critical.

The components of the color-forming system are in substantially contiguous relationship, substantially homogeneously distributed throughout the coated layer material deposited on the substrate. The term substantially contiguous is understood to mean that the color-forming components are positioned in sufficient proximity such that upon melting, softening or subliming one or more of the components, a reactive color forming contact between the components is achieved. As is readily apparent to the person of ordinary skill in this art, these reactive components accordingly can be in the same coated layer or layers, or isolated or positioned in separate layers. In other words, one component can be positioned in the first layer, and reactive or sensitizer components positioned in a subsequent layer or layers. All such arrangements are understood herein as being substantially contiguous.

In manufacturing the record material, a coating composition is prepared which includes a fine dispersion of the components of the color-forming system, binder material preferably polymeric binder such as polyvinyl alcohol, surface active agents and other additives in an aqueous coating medium. The composition can additionally contain inert pigments, such as clay, talc, silicone dioxide, aluminum hydroxide, calcined kaolin clay and calcium carbonate; synthetic pigments, such as urea-formaldehyde resin pigments; natural waxes such as Carnauba wax; synthetic waxes; lubricants such as zinc stearate; wetting agents; defoamers, sensitizers and antioxidants and p-benzylbiphenyl. The sensitizer typically does not impact any image on its own but as a relatively low melt point solid acts as a solvent to facilitate reaction between the mark forming components of the color-forming system.

The color-forming system components are substantially insoluble in the dispersion vehicle (preferably water) and are ground to an individual average particle size of between about 1 micron to about 10 microns, preferably about 1-3 microns or less. The polymeric binder material is substantially vehicle soluble although latexes are also eligible in some instances. Preferred water soluble binders include polyvinyl alcohol, hydroxy ethylcellulose, methylcellulose, methylhydroxypropylcellulose, starch, modified starches, gelatin and the like. Eligible latex materials include polyacrylates, styrene-butadiene-rubber latexes, polyvinylacetates, polystyrene, and the like. The polymeric binder is used to protect the coated materials from brushing and handling forces occasioned by storage and use of thermal sheets. Binder should be present in an amount to afford such protection in an amount less than will interfere with achieving reactive contact between color-forming reactive materials.

Coating weights can effectively be about 3 to about 9 grams per square meter (gsm) and preferably about 5 to about 6 gsm. The practical amount of color-forming materials is controlled by economic considerations, functional parameters and desired handling characteristics of the coated sheets.

Eligible electron donating dye precursors are chromogenic compounds, such as phthalide, leucauramine and fluoran compounds. Examples of the compounds include Crystal Violet Lactone (3,3-bis(4-dimethylaminophenyl)-6-dime-thylaminophthalide, U.S. Pat. No. RE. 23,024); phenyl-incol-, pyrrol-, and carbazol-substituted phthalides (for example in U.S. Pat. Nos. 3,491,111; 3,491,112; 3,491,116; 3,509,174); nitro-, amino-, amido-, sulfon amido-, aminobenzylidene-, halo-, anilino-substituted fluorans (for example, in U.S. Pat. Nos. 3,624,107; 3,627,787; 3,641,011; 3,642,828; 3,681,390); spiro- dipyrans (U.S. Pat. No. 3,971,808); and pyridine and pyrazine compounds (for example, in U.S. Pat. Nos. 3,775,424 and 3,853,869). Other specifically eligible chromogenic compounds, not limiting the invention to any way, are: 3-diethylamino-6-methyl-7-anilino-fluoran (U.S. Pat. No. 3,681,390); 2-anilino-3-methyl-6-dibutylamino-fluoran (U.S. Pat. No. 4,510,513) also known as 3-dibutylamino-6-methyl-7-anilino-fluoran; 3-dibutylamino-7-(2-chloroanilino) fluoran; 3-(N-ethyl-N-tetrahydrofurfurylamino)-6-methyl-7-3,5,6-tris(dime- thylamino) spiro [9H-fluorene-9,1', (3'H)-isobenzofuran]-3'-one; 7-(1-ethyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro[3,4-b] pyridin-5-one (U.S. Pat. No. 4,246,318); 3-diethylamino-7-(2-chloroanilino)fluoran (U.S. Pat. No. 3,920,510); 3-(N-methylcyclohexylamino)-6-methyl-7-anilino-fluoran (U.S. Pat. No. 3,959,571); 7-(1-octyl-2-methylindol-3-yl)-7-(4-diethylamino-2-ethoxyphenyl)-5,7-dihydrofuro[3,4-b] pyridin-5-one; 3-diethylamino-7,8-benzofluoran; 3,3-bis(1-ethyl-2-methylindo 1-3-yl) phthalide; 3-diethylamino-7-anilino-fluoran; 3-diethylamino-7-benzylaminofluoran; 3-phenyl-7-dibenzylamino-2,2'-spiro-di-[2H-1-benzopyran] and mixtures of any of the following.

Examples of eligible acidic developer material include the compounds listed in U.S. Pat. No. 3,539,375 as phenolic reactive material, particularly the monophenols and diphenols. Other eligible acidic developer material which can be used also include, without being considered as limiting, the following compounds: 4,4'-isopropylidenediphenol (Bisphenol A); p-hydroxybenzaldehyde; p-hydroxybenzophenone; p-hydroxypropiophenone; 2,4-dihydroxybenzophenone; 1,1-bis(4-hydroxyphenyl) cyclohexane; salicylanilide; 4-hydroxy-2-methylacetophenone; 2-acetylbenzoic acid; m-hydroxyacetanilide; p-hydroxyacetanilide; 2,4-dihydroxyacetophenone; 4-hydroxy-4, -methylbenzophenone; 4,4'-dihydroxybenzophenone; 2,2-bis(4-hydroxyphenyl)-4-methylpentane; benzyl 4-hydroxyphenyl ketone; 2,2-bis(4-hydroxyphenyl)-5-methylhexane; ethyl-4,4-bis(4-hydroxyphenyl)-pentanoate; isopropyl-4,4-bis(4-hydroxyphenyl) pentanoate; methyl-4,4-bis(4-hydroxyphenyl) pentanoate; alkyl-4,4-bis(4-hydroxyphenyl) pentanoate; 3,3-bis(4-hydroxyphenyl)pentane; 4,4-bis(4-hydroxyphenyl) pentanoate; 3, 3-bis(4-hydroxyphenyl)-pentane; 4,4-bis(4-hydroxyphenyl)-heptane; 2,2-bis(4-hydroxy-phenyl) butane; 2,2,-methylene-bis(4-ethyl-6-tertiarybutyl phenol); 4-hydroxy-coumarin; 7-hydroxy-4-methylcoumarin; 2,2,-methylene-bis(4-octylphenol); 4,4,-sulfonyldiphenol; 4,4'-thiobis(6-tertiarybutyl-m-cresol); methyl-p-hydroxybenzoate; n-propyl-p-hydroxybenzoate; benzyl-p-hydroxybenzoate. Preferred among these

are the phenolic developer compounds. More preferred among the phenol compounds are 4,4-isopropylindinediphenol, ethyl-4,4-bis (4-hydroxyphenyl)-pentanoate, n-propyl -4,4-bis (4-hydroxyphenyl) pentanoate, isopropyl -4,4-bis (4-hydroxyphenyl) pentanoate, methyl-4,4-bis(4-hydroxyphenyl) pentanoate, 2,2-bis (4-hydroxy-phenyl)-4,4-methylpentane, p-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 1,1-bis (4-hydroxyphenyl) cyclohexane, and benzyl-p-hydroxybenzoate. Acid compounds of other kind and types are eligible.

Examples of eligible acidic developer compounds for use with the invention are phenolic novolak resins which are the product of reaction between, for example, formaldehyde and a phenol such as an alkylphenol, e.g., p-octylphenol, or other phenols such as p-phenylphenol, and the like; and acid mineral materials including colloidal silica, kaolin, bentonite, attapulgite, hallosyte, and the like. Some of the polymers and minerals do not melt but undergo color reaction on fusion of the chromogen.

The invention will now be illustrated by reference to a number of Examples and to Tables 1 and 2 and Figures 1, 2, 3 and 4 of the accompanying drawings

Fig. 1 illustrates the thermal response of the thermally responsive record material of the invention wherein components are ground together compared with comparative examples 2, 3, 4, 5, 6 and 7 wherein the components are ground separately.

Fig. 2 illustrates the thermal response of the thermally responsive record material of the invention wherein components are ground together compared with comparative examples 8, 9, 10, 11 and 12 wherein the components are ground separately.

Fig. 3 illustrates the thermal response of thermally responsive record material according to the invention where components are ground together compared with comparative examples 13, 14, 15, 16 and 17.

Fig. 4 illustrates the thermal response of thermally responsive record material according to the invention where components are ground together compared with comparative examples 20, 21 and 22. Examples 1, 18 and 19 illustrate the invention.

In Tables 1 and 2 the "Examples" illustrate the invention by comparison to the "Comp. Examples" or Comparative Examples.

In this invention the various ingredients are ground together. The effect of grinding the ingredients together as compared to grinding separately is illustrated in Table 1, the comparison of Example 1 versus Comp. Examples 2 through 12. In particular the intensity improvement of Example 1 versus identically constituted but separately ground Comp. Example 7 is noted. Figures 1 and 2 illustrate the comparisons visually.

In Table 2 the Examples and the Comp. Examples, all have ingredients ground together. The criticality of the ranges of the invention are illustrated.

Examples 1, 18 and 19 illustrate the invention. These examples are presented visually in Figures 3 and 4.

Figure 3 illustrates that by grinding the ingredients together improvements in sensitivity are achieved as the various graphed lines tend toward merger.

In Figure 4 as the concentration of DMT exceeds about 70%, there is a noticeable drop in image density and speed of imaging.

In Figure 3 as DMT concentration drops below about 50% and the DPE concentration predominates, the response curve of DPE is obtained. DPE today is a commercially used sensitizer. It is surprising and unexpected that from 50 to 70% of DPE can be replaced with the combination of the invention. An intense imaging paper is obtained.

Table 1

| Parts DPE/ DMT/AP5 | Example 1 Ground Together | Comp. Example 2 Ground Separately | Comp. Example 3 Ground Separately | Comp. Example 4 Ground Separately | Comp. Example 5 Ground Separately | Comp. Example 6 Ground Separately |
|------------------------------|---------------------------------|---|---|---|---|---|
| | | | | | | |
| .5/5/1 | 50%-50% | 1/0/1 | .9/.1/1 | .8/.2/1 | .7/.3/1 | .6/.4/1 |
| 8 DPE/DMT | 50%-50% | 100%-0% | 90%-10% | 80%-20% | 70%-30% | 60%-40% |
| Head Energy | 0.08 | 0.11 | 0.08 | 0.09 | 0.07 | 0.07 |
| 3.102 (mj/mm ²) | | | | | | |
| Head Energy | 0.16 | 0.16 | 0.16 | 0.16 | 0.13 | 0.10 |
| 8.571 (mj/mm ²) | | | | | | |
| Head Energy | 0.49 | 0.53 | 0.40 | 0.39 | 0.13 | 0.29 |
| 11.633 (mj/mm ²) | | | | | | |
| Head Energy | 0.97 | 0.95 | 0.93 | 0.79 | 0.35 | 0.72 |
| 16.122 (mj/mm ²) | | | | | | |
| Head Energy | 1.19 | 1.16 | 1.13 | 1.04 | 0.76 | 0.98 |
| 19.184 (mj/mm ²) | | | | | | |
| Head Energy | 1.28 | 1.28 | 1.20 | 1.12 | 0.98 | 1.08 |
| 21.735 (mj/mm ²) | | | | | | |
| Head Energy | 1.28 | 1.25 | 1.20 | 1.14 | 1.08 | 1.08 |
| 24.082 (mj/mm ²) | | | | | | |
| Head Energy | 1.31 | 1.25 | 1.21 | 1.14 | 1.09 | 1.08 |
| 26.122 (mj/mm ²) | | | | | | |
| Head Energy | 1.30 | 1.21 | 1.23 | 1.14 | 1.10 | 1.08 |
| 29.388 (mj/mm ²) | | | | | | |
| Head Energy | 1.29 | 1.19 | 1.18 | 1.13 | 1.12 | 1.11 |
| 32.653 (mj/mm ²) | | | | | | |

Table 1 Continued

| Parts DPE/ DMT/AP5 | Comp. Example 7 Ground Separately | Comp. Example 8 Ground Separately | Comp. Example 9 Ground Separately | Comp. Example 10 Ground Separately | Comp. Example 11 Ground Separately | Comp. Example 12 Ground Separately |
|---|---|---|---|--|--|--|
| .5/.5/1 | | .4/.6/1 | .3/.7/1 | .2/.8/1 | .1/.9/1 | 0/1/1 |
| 50%-50% | | 40%-60% | 30%-70% | 20%-80% | 10%-90% | 100% |
| Head Energy 3.102 (mj/mm ²) | 0.07 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| Head Energy 8.571 (mj/mm ²) | 0.12 | 0.12 | 0.10 | 0.11 | 0.11 | 0.10 |
| Head Energy 11.633 (mj/mm ²) | 0.33 | 0.30 | 0.29 | 0.25 | 0.29 | 0.16 |
| Head Energy 16.122 (mj/mm ²) | 0.71 | 0.70 | 0.71 | 0.67 | 0.70 | 0.56 |
| Head Energy 19.184 (mj/mm ²) | 0.98 | 0.98 | 0.95 | 0.95 | 1.00 | 0.90 |
| Head Energy 21.735 (mj/mm ²) | 1.05 | 1.06 | 1.05 | 1.08 | 1.09 | 1.09 |
| Head Energy 24.082 (mj/mm ²) | 1.05 | 1.07 | 1.07 | 1.09 | 1.09 | 1.10 |
| Head Energy 26.122 (mj/mm ²) | 1.05 | 1.08 | 1.07 | 1.09 | 1.09 | 1.12 |
| Head Energy 29.388 (mj/mm ²) | 1.05 | 1.08 | 1.06 | 1.08 | 1.10 | 1.10 |
| Head Energy 32.653 (mj/mm ²) | 1.07 | 1.06 | 1.06 | 1.07 | 1.08 | 1.09 |

Table 2

| Example 1 | | Comp. Example 13 Ground Together | Comp. Example 14 Ground Together | Comp. Example 15 Ground Together | Comp. Example 16 Ground Together | Comp. Example 17 Ground Together |
|------------------------------|---------|--|--|--|--|--|
| Parts DPE/ DMT/AP5 | .5/.5/1 | 1/0/1 | .9/.1/1 | .8/.2/1 | .7/.3/1 | .6/.4/1 |
| % DPE/DMT | 50%-50% | 100%-0% | 90%-10% | 80%-20% | 70%-30% | 60%-40% |
| Head Energy | 0.08 | 0.1 | 0.08 | 0.08 | 0.08 | 0.08 |
| 3.102 (mj/mm ²) | | | | | | |
| Head Energy | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 | 0.16 |
| 8.571 (mj/mm ²) | | | | | | |
| Head Energy | 0.49 | 0.53 | 0.49 | 0.48 | 0.49 | 0.49 |
| 11.633 (mj/mm ²) | | | | | | |
| Head Energy | 0.97 | 0.95 | 0.93 | 0.96 | 0.95 | 0.97 |
| 16.122 (mj/mm ²) | | | | | | |
| Head Energy | 1.19 | 1.16 | 1.17 | 1.16 | 1.16 | 1.19 |
| 19.184 (mj/mm ²) | | | | | | |
| Head Energy | 1.28 | 1.28 | 1.27 | 1.27 | 1.26 | 1.28 |
| 21.735 (mj/mm ²) | | | | | | |
| Head Energy | 1.28 | 1.25 | 1.26 | 1.27 | 1.26 | 1.28 |
| 24.082 (mj/mm ²) | | | | | | |
| Head Energy | 1.31 | 1.25 | 1.25 | 1.27 | 1.27 | 1.31 |
| 26.122 (mj/mm ²) | | | | | | |
| Head Energy | 1.3 | 1.25 | 1.25 | 1.26 | 1.26 | 1.3 |
| 29.388 (mj/mm ²) | | | | | | |
| Head Energy | 1.29 | 1.25 | 1.25 | 1.26 | 1.26 | 1.29 |
| 32.653 (mj/mm ²) | | | | | | |

Table 2 Continued

| Example 18 | | Example 19 | Comp. Example 20 | Comp. Example 21 | Comp. Example 22 |
|------------------------------|---------|-----------------|------------------|------------------|------------------|
| Ground Together | | Ground Together | Ground Together | Ground Together | Ground Together |
| Parts DPE/ DMT/AP5 | .4/.6/1 | .3/.7/1 | .2/.8/1 | .1/.9/1 | 0/1/1 |
| % DPE/DMT | 40%-60% | 30%-70% | 20%-80% | 10%-90% | 0%-100% |
| Head Energy | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 |
| 3.102 (mj/mm ²) | | | | | |
| Head Energy | 0.17 | 0.12 | 0.12 | 0.1 | 0.1 |
| 8.571 (mj/mm ²) | | | | | |
| Head Energy | 0.35 | 0.31 | 0.25 | 0.28 | 0.16 |
| 11.633 (mj/mm ²) | | | | | |
| Head Energy | 0.75 | 0.73 | 0.68 | 0.68 | 0.56 |
| 16.122 (mj/mm ²) | | | | | |
| Head Energy | 1.01 | 0.98 | 0.96 | 0.95 | 0.9 |
| 19.184 (mj/mm ²) | | | | | |
| Head Energy | 1.11 | 1.08 | 1.09 | 1.07 | 1.09 |
| 21.735 (mj/mm ²) | | | | | |
| Head Energy | 1.14 | 1.1 | 1.09 | 1.08 | 1.1 |
| 24.082 (mj/mm ²) | | | | | |
| Head Energy | 1.13 | 1.1 | 1.1 | 1.08 | 1.12 |
| 26.122 (mj/mm ²) | | | | | |
| Head Energy | 1.13 | 1.08 | 1.09 | 1.08 | 1.1 |
| 29.388 (mj/mm ²) | | | | | |
| Head Energy | 1.11 | 1.08 | 1.08 | 1.06 | 1.09 |
| 32.653 (mj/mm ²) | | | | | |

Table 1 illustrates Example 1 of the invention wherein the components are ground together compared to comparative examples wherein the components are ground separately. Example 1 illustrates the invention. The thermal record material samples are imaged on an Atlantek imaging device. The imaged samples are then read with a MacBeth densitometer. The MacBeth image density values are graphed as thermal response curves in Figs. 1, 2, 3 and 4.

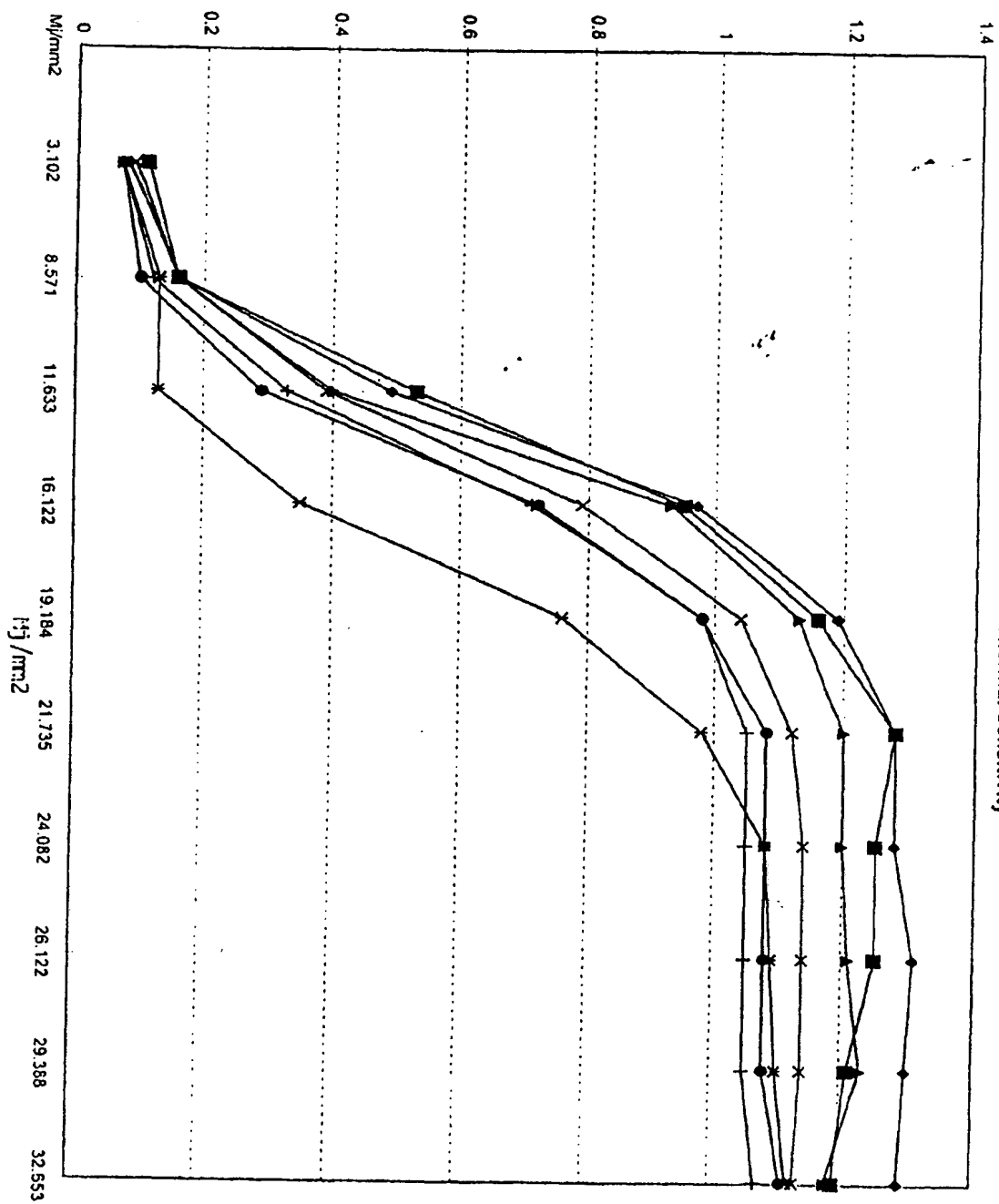
Examples 1, 18 and 19 illustrate the invention. In Figs. 1 and 2, in the comparative examples, the components are ground separately. In Figs. 3 and 4, the components are ground together.

Examples 1, 18 and 19 surprisingly have faster and more intense image density.

Claims

1. A thermally responsive record material comprising a support having provided thereon in substantially contiguous relationship in one or more layers an electron donating dye precursor, an acidic developer material, a sensitizer, and a binder therefor, characterized in that the sensitizer comprises at least two components, the first component comprising 2,2-bis(4-hydroxyphenyl)-4-methylpentane and the second component comprising a mixture of dimethyl terephthalate and 1,2-diphenoxyethane, said second component comprising from 50 to 70% dimethyl terephthalate by weight, and in that the sensitizer is prepared by admixing the first component and the second component and grinding the sensitizer to a particle size of less than 1 micron.
2. Thermally responsive record material according to claim 1, wherein the first component is in a range of weight ratios from 1:2 to 2:1 relative to the second component.
3. A thermally responsive record material according to claim 2, wherein the first component and second component are substantially equal by weight.
4. A thermally responsive record material according to any preceding claim, wherein the acidic developer material is a phenol compound.
5. A thermally responsive record material according to claim 4, wherein the acidic developer material is benzyl-p-hydroxybenzoate.
6. A thermally responsive record material according to any preceding claim, wherein the electron donating dye precursor is a fluoran compound.
7. A process for forming an improved sensitizer for thermally responsive record material comprising admixing a first component and a second component, the first component comprising 2,2-bis(4-hydroxyphenyl)-4-methylpentane and the second component comprising a mixture of dimethyl terephthalate and 1,2-diphenoxyethane, said second component comprising from 50 to 70% dimethyl terephthalate by weight, grinding the admixture to a particle size of less than 1 micron, and forming an aqueous slurry of the admixture.
8. A process according to claim 7, wherein the first component is in a range of weight ratios from 1:2 to 2:1 relative to the second component.
9. A process according to claim 8, wherein the first component and second component are substantially equal by weight.
10. The process according to any of claims 7 to 9, wherein the admixture is combined with a dye precursor and acidic developer to form a coating slurry and the coating slurry is coated onto a substrate.

Figure 1
Thermal Sensitivity



- Example 1
- Comp. Example 2
- ▲ Comp. Example 3
- × Comp. Example 4
- * Comp. Example 5
- Comp. Example 6
- + Comp. Example 7

Figure 2
Thermal Sensitivity

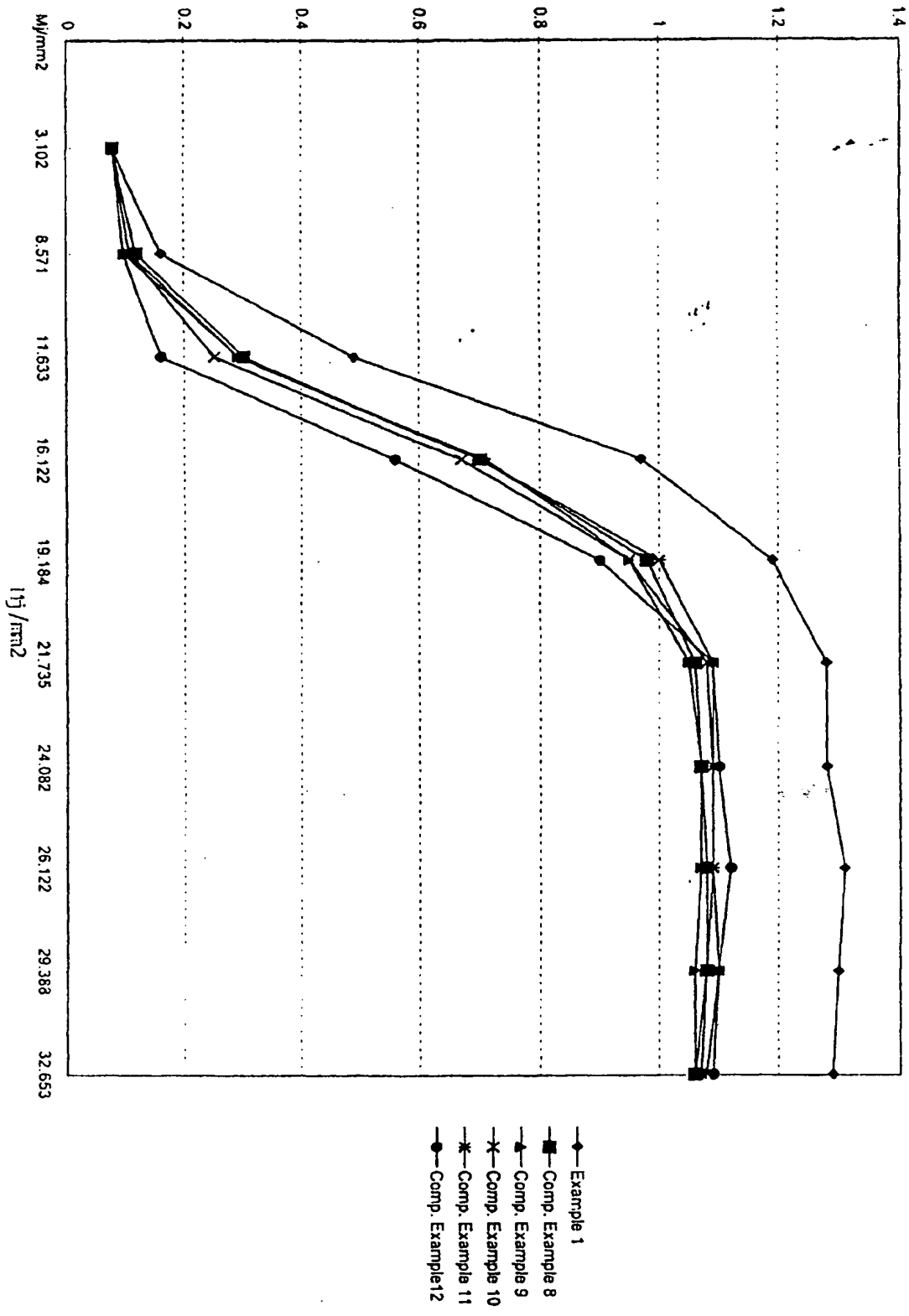


Figure 3
Thermal Sensitivity

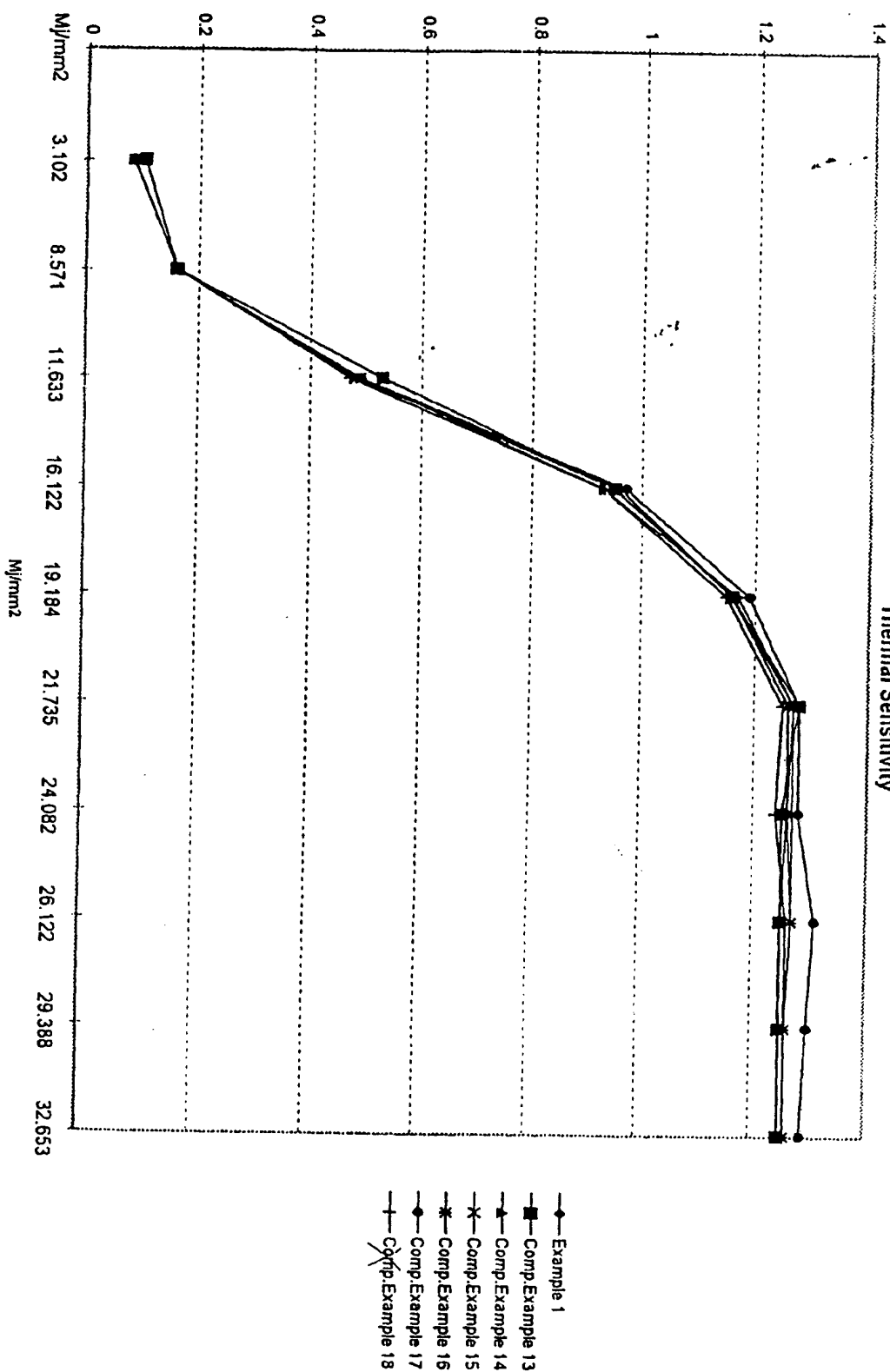
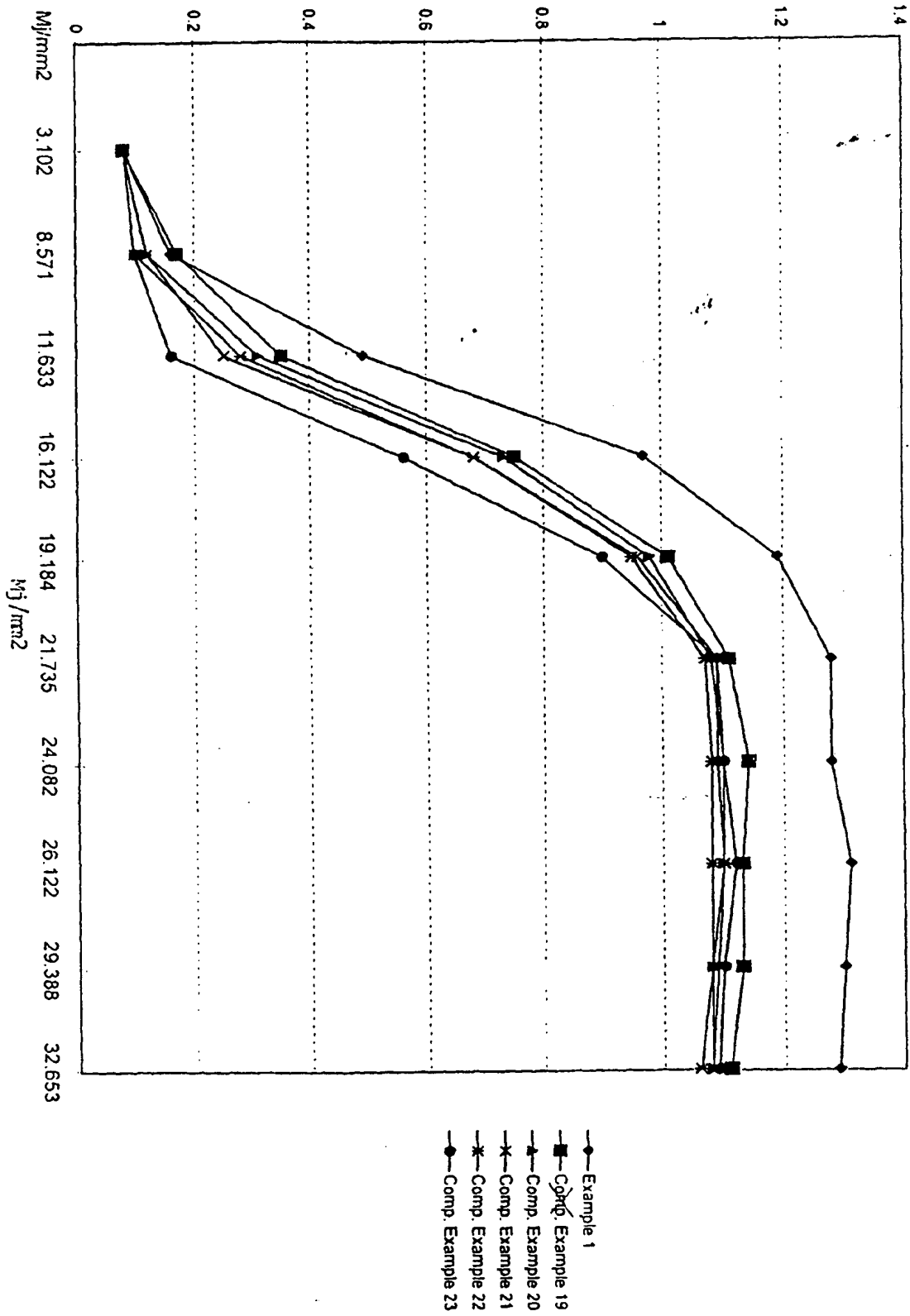


Figure 4
Thermal Sensitivity





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 30 1953

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|--|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| A | EP 0 443 805 A (OJI PAPER CO) 28 August 1991 * page 2, line 20 - page 4, line 30 * * page 5, line 9 - line 29 * * examples * | 1,7 | B41M5/30 |
| A | EP 0 343 014 A (WIGGINS TEAPE GROUP LTD) 23 November 1989 * page 2, line 14 - line 43 * * page 3, line 59 - line 65 * * page 4, line 35 - line 42 * * example 3 * | 1,7 | |
| A | US 5 124 307 A (DALEBROUX DEAN G ET AL) 23 June 1992 * column 3, line 4 - line 24 * * column 3, line 63 - column 4, line 15 * * column 6, line 9 - line 16 * * example 1 * | 1,7 | |
| A | EP 0 058 345 A (JUJO PAPER CO LTD) 25 August 1982 * page 3, line 29 - page 4, line 28 * * page 6, line 16 - line 29 * * examples * | 1,7 | TECHNICAL FIELDS SEARCHED (Int.Cl.6) B41M |
| A | FR 2 582 990 A (LABELON CORP) 12 December 1986 * page 1, line 28 - page 2, line 11 * * example * | 1,7 | |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 22 June 1998 | Examiner Markham, R |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p> | | | |

EPO FORM 1503 03/92 (P4/C01)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)